



7

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: H01B 3/40, 3/46	A1	(11) International Publication Number: WO 98/32138
		(43) International Publication Date: 23 July 1998 (23.07.98)

(21) International Application Number: PCT/HU98/00007

(22) International Filing Date: 21 January 1998 (21.01.98)

(30) Priority Data:
P 97 00191 21 January 1997 (21.01.97) HU(71) Applicant (for all designated States except US): FURUKAWA
ELECTRIC INSTITUTE OF TECHNOLOGY [HU/HU];
Késmárk u. 24-28, H-1158 Budapest (HU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BÀNHEGYI, György
[HU/HU]; Andor u. 11/a, H-1119 Budapest (HU).
PINTÉR, Szilveszter [HU/HU]; Pozsonyi út 95, H-9330
Kapuvár (HU). CSECSÓDY, Sándor [HU/HU]; Sasadi út
125, H-1112 Budapest (HU). TÉGLÁS, Márton [HU/HU];
Andrássy út 3, H-1061 Budapest (HU). BORSOS,
Zoltán [HU/HU]; Kaszásdűlő 1, H-1031 Budapest (HU).
FÖLDESI NAGY, Ilona [HU/HU]; Óda u. 26, H-1155
Budapest (HU).(74) Agent: DANUBIA; Bajcsy-Zsilinszky u. 16, H-1051 Budapest
(HU).(81) Designated States: JP, US, European patent (AT, BE, CH, DE,
DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.
Before the expiration of the time limit for amending the
claims and to be republished in the event of the receipt of
amendments.

(54) Title: ELECTRIC INSULATION COMPOSITIONS BASED ON EPOXY-SILICONE HYBRID RESINS

(57) Abstract

The essence of the disclosed composition is the combination of materials of excellent insulating properties. The cheaper price and the easy processability of epoxy resins are combined with the advantageous surface properties (hydrophobicity, recovery after dry band arcing) and good weather resistance of silicone rubbers. The new composition can be processed by low pressure casting or by pressure gelation. Due to its low viscosity the base resin can take up a large amount of fillers. The silicone component modifying the epoxy resin is not simply a plasticizer, but it is built into the network structure and its effect is permanent. The main components of the composition are cycloaliphatic, aliphatic (or aromatic) epoxy resin, cycloaliphatic (or aromatic) anhydride (perhaps amine or polyamino-amide) cross-linker, accelerator, and a silicone oligomer containing epoxy end-group. Further components may be low molecular or macromolecular active diluent (flexibilizer) and filler. By changing the ratio of the components one can produce several compositions from a rigid, load-bearing structure up to the soft, rubber-like structures.

1) epoxy (7-epikler (cyclo)aliphatic)
2) hardener (anhydride; amine or polyamino-amide)
3) epoxy-silicone (poly-siloxane)

u. 1.97 12 u. 1.98 12 u. 1.99 16 ↓
98 99

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Electric insulation compositions based on epoxy- silicone hybrid resins

The invention relates to an insulating composition the resin component of which contains reactive silicone oligomers besides epoxy resin and other, known components, so it unites the advantageous properties of both insulating materials.

The application of epoxy resins for electrical insulation has been known for a long time. Besides their advantageous properties (as high mechanical and electrical strength, heat and chemical resistance) they have some disadvantages as well (as cracking, and disappearance of surface hydrophobicity after long term outdoor exposure or after dry band arcing etc.). It is also known that for outdoor applications cycloaliphatic resin and anhydride is preferable to aromatic ones due to their better weather and electrical erosion resistance. Cycloaliphatic resins are less prone to tracking in the case of dry band arcing.

In the past years silicones and silicone rubber based composite insulators gradually gain leading role in outdoor insulation. The main reason for this is the hydrophobicity of silicone rubber, which prevents the formation of a continuous water film on the insulator surface, thus reducing the leakage current, and the erosion caused by dry band arcing. One of the advantages of silicone rubbers is that this hydrophobic property is stable for a long time, moreover, if it is destroyed temporally due to weather circumstances or to discharges, it gradually recovers afterwards. The reason for this hydrophobic recovery is in part the

migration (diffusion) of low molecular silicone oils to the surface, and in part the re-orientation of the silicone chains located at the surface.

Because of the advantageous properties of these materials there have been attempts to unite them in various compositions. The patented combinations frequently emphasize the good electrical insulation, the heat- and weather resistance of the compositions. JP 05271518 e.g. uses a mixture of alkyphenol-polysiloxane block copolymers with bisphenol-A type epoxy resins. JP 05301931 proposes a mixture of siloxane grafted vinyl polymers in combination with cresol- or novolak type epoxy resins. JP 05160173 reacts maleimide end-functionalized siloxane with epoxidized polybutadiene. JP 05105778 combines carboxyl end functionalized nitrile rubber with amine end-functionalized siloxane and epoxy, and there are further examples. All these compositions use special, commercially not available components.

Other patents, as e.g. JP 62243649, CS 217338, US 4537803, JP 60112814, JP 52068248, US 3843577 describe compositions containing low molecular (mobile) silicone oil additive in order to improve hydrophobicity, weather resistance or partial discharge properties, but these oils are not built into the network of the epoxy resin.

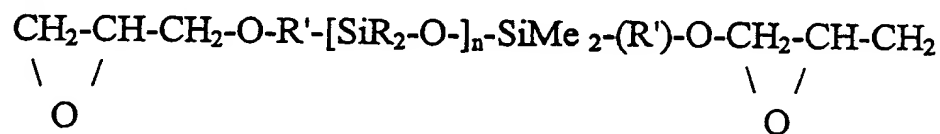
Our goal with this invention was to develop epoxy resin compositions from commercially available components, which:

- 1) contain the silicone component incorporated into the network, thus it cannot be removed from the system, its effect is permanent;
- 2) are cheaper than the HTV (high temperature vulcanizing) or LSR (liquid silicone rubber) materials used in insulator production;

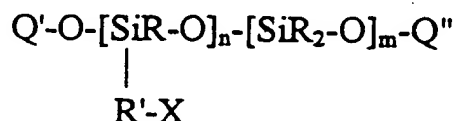
3) can be processed by low- or medium pressure liquid technology even with high filler content.

During the development the following ideas were utilized

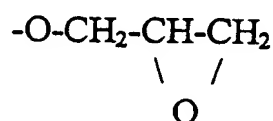
- 1) A proper combination of thermoset resins (so called hybrid resins) can unite the advantageous properties of both components (see e.g. the urethane – unsaturated polyester hybrids). These are not physical mixtures, as e.g. the blends of thermoplastics, but copolymers (block or statistical copolymers).
- 2) In the past few years several reactive silicone oligomers appeared on the market in which the reactive group (hydroxyl, amine, acrylate, epoxy etc.) is not attached directly to the silicon atom, but through a saturated propylene $[-(\text{CH}_2)_3-]$ or butylene $[-(\text{CH}_2)_4-]$ bridge. These intermediates are chemically stable, can be stored for a long time. Their functional end-groups enable them to be incorporated as dimethyl siloxane blocks into other, thermoset resins. The chemical composition of commercially available epoxy-modified silicone oligomers is as follows:



where R' is a saturated hydrocarbon chain. At a laboratory scale other structures can also be easily synthesized which contain the epoxy group in the side chain, such as:



where R is an alkyl group, Q' and Q'' can be trimethyl silyl group (-SiMe₃) or an -R'-X group, where R' is a saturated hydrocarbon chain and X is a glycidoxyl group:



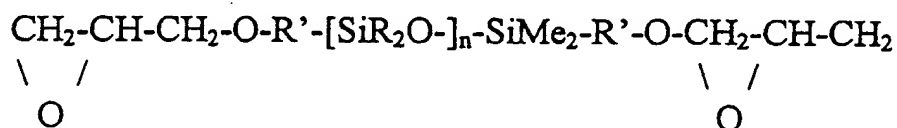
- 3) If a statistical or block copolymer contains about 10% siloxane units, then the surface energy of the copolymer will be similar to that of typical siloxane polymers (i.e. it will be hydrophobic), as the surface will become rich in the low surface energy siloxane component.

Based on the above ideas the invention proposes a group of hybrid resins characterized by mixture of traditional epoxy resins with siloxane oligomers containing epoxy functional groups and with a calculated amount of crosslinker.

Accordingly, the invention relates to epoxy resin based insulating composition with improved hydrophobicity and electrical erosion resistance that comprises a cycloaliphatic or aliphatic (or aromatic) epoxy resin, a cycloaliphatic (or aromatic) anhydride (perhaps amine or poly amino-amide) crosslinker comprising a silicone additive containing

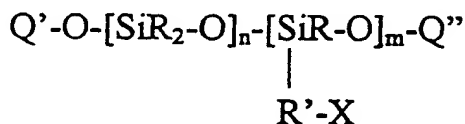
epoxy groups, occasionally in combination with polymeric active diluent (flexibilizer), reinforcing (Aerosil, wollastonite, chopped glassfiber) and/or non-reinforcing (silica, ATH, calcium carbonate, baryte) fillers and a mobile silicone oil, not bound to the network.

In the compositions according to the invention the siloxane oligomer containing epoxy functional groups is preferably a polysiloxane (wherein R may be methyl or phenyl) with the glycidyl group attached in the following way:

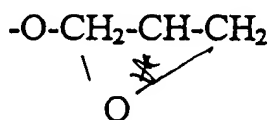


where R' is a saturated hydrocarbon chain with 1-10, preferably with 3-4 carbon atoms and n, the degree of polymerization is between 1 and 50, preferably between 5 and 15,

or a polysiloxane having the following formula:



where R is methyl or phenyl, m+n, the degree of polymerization is between 1 and 50, preferably between 5 and 15, m is between 1 and 5, preferably 1 or 2, Q' or Q'' may be trimethyl silyl group (-SiMe₃) or an -R'-X group, where R' is a saturated hydrocarbon chain with 1-10, preferably with 3-4 carbon atoms and X is the glycidoxyl group:



It is advantageous if the resin and the crosslinker components are miscible with the siloxane oligomer. The selection of such components is by no means trivial, as, due to the extremely low cohesion energy density of polysiloxanes, they are not miscible with all organic liquids. If the siloxane oligomer is miscible with the crosslinker but not with the epoxy resin then the siloxane phase may crosslink separately from the epoxy matrix. This is called macroscopic phase separation (two layers of separated materials appear), which results in a technically unacceptable product. One has to distinguish this situation sharply from micro phase separation, which occurs during block copolymer synthesis. In this process the monomers or oligomers, which are miscible at the molecular level in the original state, become separated during the polymerization due to the decrease of mixing entropy. As, however, the blocks are linked chemically to each other phase separation remains microscopic. Micro phase separation contributes to the special set of properties of block copolymers.

In the case of outdoor insulations the epoxy component is advantageously cycloaliphatic epoxy and the crosslinker is a cycloaliphatic anhydride (both low viscosity liquids at room temperature). If the epoxidized siloxane is mixed with the cycloaliphatic epoxy in a ratio of 1:9 and is crosslinked with a calculated amount of crosslinker, then a polymer with siloxane-like surface properties is

obtained. The electrical erosion resistance can be improved by the addition of aluminum oxide trihydrate (ATH) filler and the flexural modulus and the tensile strength can be substantially increased by anisometric fillers (chopped glassfiber, wollastonite or other, whisker-like filler). Cheap, extender fillers (as e.g. silica or calcium carbonate) can reduce the price. This composition can be a competitor of traditional, silica filled cycloaliphatic casting resins. In this case the hybrid resin is a load-bearing component, which can be fixed onto the electrical network through embedded metal fittings. The advantage of this composition over the traditional casting resins is the silicone rich, hydrophobic surface, which can recover its hydrophobicity after oxidation.

Compositions containing both epoxidized silicone oligomer (immobile silicone component) and a low molecular silicone oil (mobile silicone component) are also possible. The immobile silicone component by itself ensures the required surface properties and the hydrophobic recovery after surface oxidation, but, if a mobile silicone component is also present then the even the inorganic deposit (dust etc.) on the insulator surface becomes hydrophobic. The immobile silicone component plays an important role even in such compositions for two reasons. A.) the mobile silicone component can be added to the epoxy resin only in a very limited amount, as, due to incompatibility problems it is easily exuded to the surface. B.) mobile silicone can be gradually depleted in the sample due to migration, but the immobile silicone content is stable.

Based on the above system it is possible to construct softer, more flexible compositions which, in principle, could be used to replace silicone rubber in the manufacture of composite outdoor insulators. In these compositions the rigidity of the epoxy resin component can be reduced by the addition of active diluents (advantageously polymeric active diluents). Active diluents are special plasticizers, which are incorporated into the epoxy network and reduce its rigidity. Flexibilization is achieved either by reducing the degree of crosslinking (low molecular, monofunctional epoxy compounds) or by incorporating soft segments into the rigid network. One example of polymeric active diluents is a glycidoxyl end functionalized polyether oligomer. The application of polymeric active diluents is necessary for two reasons: a.) the siloxane network by itself is not too strong (although it can be considerably reinforced by the addition of silica gel of pyrolytic origin, e.g. Aerosil or Cab-O-Sil), therefore the increase of the siloxane/epoxy resin ratio does not yield a system of advantageous mechanical properties; b.) the siloxane oligomer is usually more expensive than the polymeric active diluent. The active diluent shall be chosen so that it is miscible with the siloxane oligomer and the other initial, liquid components. Similarly to the previous system, it is advantageous to use cycloaliphatic resin and additives improving the electrical erosion resistance (e.g. ATH). The advantage of this system over silicone rubber is its lower price and (at a similar filled loading level) the significantly lower viscosity.

The amount of the crosslinker, which is applied in a stoichiometric quantity, can be calculated by the following formula:

$$T = (xe_1 + ye_2 + ze_3)/A$$

where x is the weight of the epoxy resin, e_1 is the specific epoxy content of the resin (mole epoxy group/100 g resin, which can be calculated from the epoxy equivalent, E by the following formula: $100/E$), y is the weight of the epoxidized silicone, e_2 is its specific epoxy content, z is the weight of the active diluent, e_3 is its specific epoxy content and A is the specific functional group content of the crosslinker (e.g. anhydride) in mol/100 g units.

The invention is illustrated by the following examples.

Example 1

Proof of the reaction between the epoxidized silicone and the cycloaliphatic anhydride

Calculated amounts (see Table 1) of cycloaliphatic anhydride (Lekutherm Härter M, Bayer AG, anhydride equivalent 168 g) and a silicone oligomer containing epoxy end-group (Tegomer ESi-2130 and ESi-2330, TH Goldschmidt AG, epoxy equivalents 514 and 1254 respectively) are mixed together. The components are fully miscible. These mixtures consolidate within 1 day at room temperature and yield a rubbery mass. The transmission IR spectrophotometric investigation of the reactants and of the products proves unambiguously the reaction between the components. (The doublet, characteristic of cyclic anhydrides, appearing at 1780 and at 1860 cm^{-1} disappears and an ester carbonyl, which is the result of the reaction between the anhydride and

the epoxy group, appears at 1740 cm^{-1} .) The reaction of the anhydride group can be regarded as complete.

Table 1
Weight portions of the components

Formulation	ESi-2130	ESi-2330	Härter M
1.	100	-	32.8
2.	-	100	14.3

Example 2

Synthesis of epoxy-silicone hybrids

Calculated amounts of cycloaliphatic epoxy resin (Lekutherm X100 of Bayer AG, epoxy equivalent 170-180), epoxidized silicone oligomer (Tegomer ESi-2130 or ESi-2330 of TH Goldschmidt AG) and cycloaliphatic anhydride crosslinker (Lekutherm Härter M, Bayer AG) are mixed so that the weight ratio of the components containing epoxy group is 1:1. The mixture of the reactants is in both cases homogeneous. In order to accelerate the reaction DMP-30 accelerator is added (0.5 wt% of the X100 epoxy component). The gel time is measured at 100°C by Gelnorm instrument, which determines the time required reaching a certain viscosity. Table 2 shows the formulations and the corresponding gel times. In the case of Tegomer ESi-2130 a solid product is obtained, while in the case of ESi-2330 macroscopic phase separation occurs.

Table 2
Compositions and gel times

Formulation	ESi-2130	ESi-2330	Härter M	Lekutherm X100	Gel time at 100 °C
3.	50	-	66.4	50	61 min
4.	-	50	56.7	50	35 min

Example 3

Variation of hybrid component composition, proof of the appearance of silicone rich surface

Calculated amounts of cycloaliphatic epoxy resin (Lekutherm X100 of Bayer AG, epoxy equivalent 170-180), epoxidized silicone oligomer (Tegomer ESi-2130 of TH Goldschmidt AG) and cycloaliphatic anhydride crosslinker (Lekutherm Härter M, Bayer AG) are mixed so that the weight ratio of the components containing epoxy group is 3:1, 1:1 and 1:3 (see Table 3). The mixture of the reactants is homogeneous in every case. If the epoxidized silicone component is in majority, a translucent, rubber-like material is obtained, while in the other two cases opaque, solid resins are obtained. Attenuated total reflectance (ATR) IR spectra, which probe the top 0.1 μm thick layer of the sample, the ratio of the band intensities (baseline corrected peak absorbance values) attributable to the ester (1740 cm^{-1}) and to the Si-Me (1260 cm^{-1}) groups is roughly identical for all three compositions (a change of 20-30% can be observed), while the molar ratio of the ester/dimethyl silicone groups changes almost tenfold. This proves the

fact, known also from the literature, that the low surface energy silicone units mainly determine the surface properties of copolymers containing dimethyl siloxane monomers (especially blocks).

Table 3
Weight ratios of the components

Formulation	ESi-2130	Lekutherm 100	Härter M
5.	50	150	166.4
3.	100	100	113.4
6.	150	50	99.4

(The composition of the 1:1 mixture is identical with composition 3. of Example 2.)

Example 4

The effect of silicone additive and of mineral fillers on the electrical erosion properties of hybrid resins

In order to check the effect of epoxidized silicone additive and of fillers on the compound properties 4 formulations were prepared (see Table 4.a.), where the amounts of the epoxidized silicone additive and of the fillers (silica and/or ATH) was varied. The mixtures containing fillers were thoroughly mixed in a Molteni type vacuum mixer, evacuated, then poured into a casting mold and cured at 100 °C. Test samples were cut from the sheets and the inclined plane electrical erosion test (IEC 587) was performed on them. The results are summarized in Table 4.b. 5 parallel samples were investigated. At a given voltage level all 5 samples must survive for at least 6 hours. The

measurement of a given sample is terminated if the leakage current measured on it exceeds 60 mA. The table also indicates the mode of failure (overcurrent without carbonization /tracking/, overcurrent with carbonization, overcurrent with fire). As shown by the table that the basic, silica filled composition without silicone additive is not acceptable even at 3.5 kV. Dramatic improvement can be observed on addition of the silicone additive. The overcurrent appearing at 4.5 kV does not cause carbonization or fire, therefore it cannot be regarded as serious damage. An improvement can be observed if no silicone additive is used but ATH is added instead of silica as filler. In this latter case the arc-suppression ability of ATH is observed, not the effect of surface hydrophobicity. Both additives together are also effective, but from these formulations No. 9 proved to be the best.

Table 4a

Weight ratios of the components

Formulation n	Lekutherm X100	Härter M	ESi-2130	Silica	ATH
7.	100	100	-	100	-
8.	100	100	-	-	100
9.	75	99.6	75	225	-
10.	75	99.6	75	-	225

Table 4b

Lifetimes of the compositions described in the previous table as
measured by IEC 587 inclined plane test

Formulation	3.5 kV	4.5 kV
No. 7.	68 min (burning)	8 min (burning)
Filler: silica	68 min (burning)	10 min (burning)
Silicone additive: none	59 min (burning)	12 min (burning)
	43 min (overcurrent)	32 min (overcurrent)
	52 min (carbonization)	57 min (burning)
No. 8.	216 min (overcurrent)	88 min (overcurrent)
Filler: ATH	360 min	94 min (overcurrent)
Silicone additive: none	360 min	360 min
	360 min	360 min
	360 min	360 min
No. 9.	360 min	105 min
Filler: Silica	360 min	360min
Silicone additive: yes	360 min	360 min
	360 min	360 min
	360 min	360min
No. 10.	186 min (overcurrent)	99 min (overcurrent)
Filler: ATH	360 min	265 min (overcurrent)
Silicone additive: yes	360 min	360 min
	360 min	360 min
	360 min	360min

Example 5

Compositions containing various fillers, flexibilizers and epoxidized silicone

The compositions described below contain the following components: CY184 cycloaliphatic epoxy resin (Ciba Geigy), HY1102 cycloaliphatic anhydride (Ciba Geigy), DY062 accelerator (Ciba Geigy), Tegomer ESi2130 epoxidized silicone (TH Goldschmidt AG), Eupox RV-F polymeric active diluent (flexibilizer, Schering/WITCO), W12EST silica filler (Quarzwerte GmbH), ATH filler (methyl silane treated, Solem GmbH). Table 5.a shows the compositions of the compounds, while Table 5.b shows some physical quantities. If the overcurrents not leading to carbonization (tracking) or to burning are neglected, then all compositions pass the IEC 587 inclined plane test at 3.5 kV, only the average weight losses are somewhat different. Taking into account the standard deviation, however, even these differences are not significant. In the case of compositions 14-16 no weight loss, but weight increase was observed after the inclined plane test, which is the result of erosion loss (negative) and water uptake (positive). One can see from Table 5.b that the epoxidized silicone additive decreases the hardness of the resin but it does not improve the impact properties. This disadvantage can be compensated for by the addition of polymeric active diluents. This latter additive can also modify the resin composition to be more similar to hard rubbers.

Table 5a
Weight ratios of the components

Formula tion	CY184	HY1102	DY062	RV-F	ESi2130	Silica	ATH
11.	63	65	0.35	-	7	70	70
12.	56	60	0.35	7	7	70	70
13.	70	70	0.35	-	-	70	70
14.	30	43	0.35	-	40	70	70
15.	30	43	0.35	20	20	70	70
16.	30	43	0.35	40	-	70	70

Table 5b
**Some physical characteristics of the compositions shown in the
previous table**

Formulation	Impact strength Charpy, kJ/m ²	Shore D hardness
11.	3.6	85
12.	3.8	84
13.	3.8	94
14.	3.4	74
15.	5.4	76
16.	> 26	52

Example 6

Physical properties of various hybrid resin compositions containing various fillers, mobile and immobile silicone additives

Several physical properties (Table 6b) of five different formulations (see Table 6a) containing silica and other fillers with and without mobile and immobile silicone additives were compared. The cycloaliphatic epoxy component was CY184 (Ciba Geigy), the crosslinker was a cycloaliphatic anhydride (HY1102 of Ciba Geigy), the accelerator was DY062 (Ciba Geigy), the epoxidized silicone additive was Tegomer ESi-2130 (TH Goldschmidt AG), the active diluent was Eurepox RV-F (Schering/WITCO), silica filler was W12 EST (Quarzwerte GmbH), ATH was methyl silane treated grade of Solem GmbH, while wollastonite (Ca-silicate) was a non-treated grade of Quarzwerte GmbH. Table 6.a shows only the resin and the additive components, the crosslinker was the stoichiometric quantity calculated from the epoxy equivalents of the components. Formulations 19 and 21 contain 0.1 wt% mobile silicone oil (polydimethyl siloxane with 100 cP viscosity). The 0.1 wt% is calculated for the organic components without mineral filler. Formulation 17 is the reference, formulation 18 contains the same amount, but mixed filler, formulation 19 contains mobile silicone oil but no epoxidized silicone additive, formulation 20 contains the epoxidized additive but no mobile silicone oil, while formulation 21 contains both types of silicones. As shown by Table 6b, the replacement of silica by softer fillers, such as ATH, reduces the impact and the tensile strength values, although later we demonstrated that by using epoxy-silane treated ATH and wollastonite grades it is

possible to formulate resins with properties similar to the silica filled grade at equal filler content. The addition of mobile or immobile silicone oil to the system somewhat reduces the heat resistance, but the electric breakdown strength remains intact. Formulation 17 did not pass the IEC 587 inclined plane test at 3.5 kV, which is a usual requirement for outdoor insulating materials. All other formulations, containing ATH passed the test. The advantage of the epoxidized silicone additive is shown by the reduced number of overcurrent events during the test.

Table 6a**Weight ratios of the components**

Formulation	CY184	ESi-2130	Silica	ATH	Wollastonite	Silicone Oil
17.	10	-	25	-	-	-
18.	10	-	5	15	5	-
19.	10	-	5	15	5	0.1%
20.	9	1	5	15	5	-
21.	9	1	5	15	5	0.1%

Table 6b

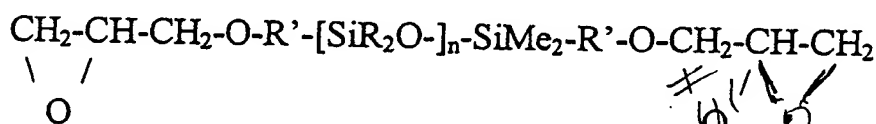
Physical properties of the compounds shown in the previous table

Formulation	No. 17.	No. 18.	No. 19.	No. 20.	No. 21.
Impact strength Charpy, kJ/m ²	12.3	4.2	5.4	4.8	4.7
Hardness Shore D	92	91	90	90	90
Tensile strength, N/mm ²	71.3	33.9	40.8	36.8	42.1
Elongation to break, %	3.3	3.1	2.5	2.3	2.6
Martens heat resistance, °C	129	128	123	115	117
No. of samples passing IEC 587 at 3.5 kV	3	5	5	5	5
No. of overcurrent events at 3.5 kV	10	7	8	2	1
Breakdown strength (kV/mm)	19.3	19.5	21.3	20.4	21.6

Claims:

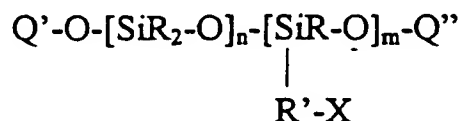
1. Epoxy resin based insulating composition with improved hydrophobicity and electrical erosion resistance that comprises a cycloaliphatic or aliphatic (or aromatic) epoxy resin, a cycloaliphatic (or aromatic) anhydride (perhaps amine or poly amino-amide) crosslinker, characterized by the presence of a silicone additive containing epoxy groups, occasionally in combination with polymeric active diluent (flexibilizer), reinforcing (Aerosil, wollastonite, chopped glassfiber) and/or non-reinforcing (silica, ATH, calcium carbonate, baryte) fillers and a mobile silicone oil, not bound to the network.

2. Epoxy resin based composition according to claim 1, characterized by that the silicone additive containing epoxy groups is a poly-siloxane (wherein R may be methyl or phenyl) with the glycidyl group attached in the following way:

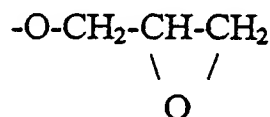


where R' is a saturated hydrocarbon chain with 1-10, preferably with 3-4 carbon atoms and n, the degree of polymerization is between 1 and 50, preferably between 5 and 15.

3. Epoxy resin based composition according to claim 1, characterized by that the silicone additive containing epoxy groups is a poly-siloxane described by the following general structure:



where R is methyl or phenyl, $m+n$, the degree of polymerization is between 1 and 50, preferably between 5 and 15, m is between 1 and 5, preferably 1 or 2, Q' or Q'' may be trimethyl silyl group ($-\text{SiMe}_3$) or an $\text{R}'\text{-X}$ group, where R' is a saturated hydrocarbon chain with 1-10, preferably with 3-4 carbon atoms and X is the glycidoxyl group:



4. Epoxy resin based composition according to claim 2 or 3 characterized by that the mass ratio of the cycloaliphatic epoxy component and of the epoxy group containing silicone additive is between 100:1 and 100:30, preferably between 100:5 and 100:20 and the amount of the crosslinker depends on the concentration of the epoxy groups, and it is added in stoichiometric amount).

5. Epoxy resin based composition according to claim 4 characterized by that the mass ratio of the total amount of the (epoxy resin + epoxy group containing silicone additive + polymeric active diluent) and the total amount of fillers is between 5:1 to 1:5, preferably between 1:1 and 1:3.

6. Epoxy resin based composition according to claim 5 characterized by that, if the total amount of fillers is 100%, the ATH content is between 20 and 60%, preferably between 40 and 50%.

7. Epoxy resin based composition according to claims 5 or 6 characterized by that, if the total amount of fillers is 100%, the content of reinforcing fillers (wollastonite and/or chopped glassfiber) is between 10 and 60%, preferably between 30 and 50%.

8. Epoxy resin based composition according to claims 5 to 7 characterized by that, if the total amount of organic components is 100%, it contains 0.5-10%, preferably 1-3% mobile silicone oil (not bound to the network).

9. Epoxy resin based composition according to claim 2 or 3 characterized by that if the total mass of the (epoxy resin + polymeric active diluent + epoxy group containing silicocne additive) is 100%, then the amount of the polymeric active diluent is 10-50%, preferably 20-40%, the amount of the epoxy group containing silicone additive is 5-50%, preferably 10-30%.

10. Epoxy resin based composition according to claim 9 characterized by that the mass ratio of the total amount of the (epoxy resin + epoxy group containing silicone additive + polymeric active diluent) and the total amount of fillers is between 5:1 to 1:5, preferably between 1:1 and 1:3.

11. Epoxy resin based composition according to claim 10 characterized by that, if the total amount of fillers is 100%, the ATH content is between 20 and 60%, preferably between 40 and 50%.

12. Epoxy resin based composition according to claims 10 or 11 characterized by that, if the total amount of fillers is 100%, the content of reinforcing filler (Aerosil) is between 1 and 10%, preferably between 2 and 5%.

13. Epoxy resin based composition according to claims 10 to 12 characterized by that, if the total amount of organic components is 100%, it contains 0.5-10%, preferably 1-3% mobile silicone oil (not bound to the network).

INTERNATIONAL SEARCH REPORT

International Application No

PCT/HU 98/00007

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 H01B3/40 H01B3/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 673 957 A (MITSUBISHI ELECTRIC CORP) 27 September 1995 see claims 1-16; example 15	1
A	US 5 358 904 A (MURAKAMI GEN ET AL) 25 October 1994 see column 47, line 12; table 1	
A	US 5 306 747 A (ITO HIROMI ET AL) 26 April 1994	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 May 1998

Date of mailing of the international search report

27/05/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Stienon, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

In ational Application No

PCT/HU 98/00007

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0673957	A	27-09-1995	JP 7242732 A	19-09-1995
			CN 1110977 A	01-11-1995
US 5358904	A	25-10-1994	JP 2246125 A	01-10-1990
			JP 2702219 B	21-01-1998
			JP 2083962 A	26-03-1990
			JP 2708191 B	04-02-1998
			US 5530286 A	25-06-1996
			US 5612569 A	18-03-1997
			US 5068712 A	26-11-1991
US 5306747	A	26-04-1994	JP 2028213 A	30-01-1990
			JP 2011654 A	16-01-1990
			JP 2608107 B	07-05-1997
			US 5157061 A	20-10-1992